DEHYDRATION OF NATURAL GAS ON ZEOLITE

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Dehydration of Natural Gas on Zeolite

By

Shameen Aida Binti Kamarulzaman

Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

_____

(Dr Nurhayati Binti Mellon)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SHAMEEN AIDA BINTI KAMARULZAMAN

ABSTRACT

Zeolite is a type of adsorbent used to dehydrate natural gas. Modifications were done to increase the adsorption capacity of zeolite. However, the current research focus more on low pressure process which might not be applicable with real condition of industrial scale. Hence, this research is carried out to investigate the zeolite capability for adsorption processes at high pressure condition which reflects the actual offshore operating condition. The experiment is carried out using GASTU and the range of operating condition of interest is from 10 bars to 80 bars of pressures and temperature ranging from 10 °C to 80 °C. Characterization of the chosen adsorbent will also be carried out to analyze the pore size, surface area, pore volumes, pore diameter, crystal form, structural information and information on hydroxyl groups attached to the adsorbent. Results shows that the micropore volume is 6.654 cm^3/g while the surface area of the adsorbent is 28.959 m^2/g. According to Brunauer definition, the chosen adsorbent has been categorized as Type I isotherms. The mean pore diameter of the adsorbent is 11.412 nm. Besides that, there are three elements attached to adsorbent having different diameters. Then, from dehydration of natural gas on zeolite experiment, the adsorption capacity increases with pressure. In conclusion, this research has shown that the chosen zeolite possesses high adsorption capacity which might favor adsorption to occur at effective rate.

ACKNOWLEDGEMENT

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Regards,

Shameen Aida Binti Kamarulzaman

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CHAPTER 1

INTRODUCTION

1. BACKGROUND

Natural gas is a naturally occurring fuel found in oil fields. Globally, natural gas is a vital component of energy supply as increasing in energy consumption leads to increasing natural gas production. Over the past 25 years, oil and gas industry have seen a remarkable growth in the contribution of the gas to the world's total primary energy demand (M. John, 2003; W. Daniel, A. Kemp, 1998).

Natural gas is a mixture of gaseous hydrocarbons and impurities. Natural gas that is used by consumers is almost pure methane. However, natural gas from the offshore is not consists of pure methane and is transported through pipelines to the onshore for further processing. Gas processing involves the removal of carbon dioxide, hydrogen sulfide, and water. Most important, these impurities must be removed before it reaches the market place to ensure good-quality sales gas.

Natural gas contains significant amount of water vapor, which condense and form solid ice-like crystals called hydrates as temperature and pressure changed. Existence of water vapor in a natural gas stream can cause line plugging due to the hydrate formation, line capacity reduced due to the collection of free water in the pipeline, and increased risk of damage to the pipeline due to the corrosive effects of water in the presence of acid gas.

Condensed liquid accumulated in pipelines, may cause an increase in operating pressure and potential damage to equipment due to liquid carryover (H. Robert et.al, 2008, P. Gandhidasan et.al. 2001, & Kh. Mohmadbeigy et.al, 2007). Therefore, water vapor must be removed from the natural gas to prevent hydrate formation and corrosion from condensed water.

Table 1: Typical Composition of Natural Gas

Type of Gas	Formula	Composition
Methane	CH_4	70-90%
Ethane	C_2H_6	70-90%
Propane	C_3H_8	0-20%
Butane	C_4H_{10}	0-20%
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen Sulphide	H_2S	0-5%
Rare Gases	A, He, Ne, Xe	Trace

Figure 1: Hydrates Removed From Pipeline

Thus, to avoid hydrate formation and pipeline corrosion,dehydration process is a must for natural gas in order to bring the water content to the specific value of dew point for the gas. Dehydration itself is a process of removing water vapor from the gas stream to lower the dew point temperature of the gas. Natural gas dehydration plants have been operating world-wide on a variety of technologies and in a number of variations for many years. There are different techniques employed for dehydrating natural gas, but only two types of dehydration techniques are commonly used in current technology which is absorption by liquid desiccant and adsorption by solid desiccants (S. Ranjani et.al, 2005). Simone Cavenati, et.al, (2004) has point out that separation and purification of gas mixtures by adsorption has become a major unit operation in chemical and petrochemical industries nowadays.

In industrial natural gas dehydration, molecular sieves are considered as one of the most important materials that are used as desiccant.Molecular sieves contain a uniform network of crystalline pores and empty adsorption cavities. Because of its uniform structure, molecular sieve will not give up moisture into the package as temperature rise (W. Vyalkina et.al., 1990). There are several types of molecular sieves that are commercially used in current technologies such as 3A, 4A, 5A, and 13X.

Nowadays, the adsorption process has been greatly researched all around the world due to its flexibility and many undiscovered and undefined aspects of adsorption. As such, the optimum conditions for adsorption reaction for different methods have been greatly researched including by using different kind of molecular sieves as the adsorbents. Currently, physical adsorption on zeolite has been identified as a potential alternative for dehydration technology due to its capability to reduce the emission and environmental effects.

2. PROBLEM STATEMENT

The formations of hydrates will block the pipeline flow especially control systems. These will cause flow restrictions, pressure drops, lower the heating value of gas and corrode pipelines and other equipment. Hence, removal of the water vapor from the natural gas is a must as to prevent the hydrate formation throughout the system and to protect the system from corrosion.

Among the choices of techniques to dehydrate the natural gas, adsorption on zeolite had been chosen because of the capability of the zeolite itself. Zeolite is a microporous material with uniform pore dimensions which allow excellent separations to be occurred and it has high selectivity with respect to water vapor. Furthermore, the strong electrostatic field within a zeolite cavity results in very strong interaction with polar molecules such as water. However, there a lot of commercial zeolites introduce in adsorption technology such as 3A, 4A, 5A and 13X. But not all of them can be operated under high pressure and temperature condition which in the normal operating condition for offshore operation. Thus, this research is carried out to investigate the adsorption capacity of chosen zeolite at high pressure and temperature.

3. OBJECTIVES

The main objective of the research is to remove water vapor from the natural gas. Besides that, the project wants tohighlight on the study of the adsorption parameter of chosen adsorbent in terms of natural gas dehydration at offshore operating conditions which can up to 70 degree Celcius for temperature and pressure at 80 bars.

After that, the optimum conditions of the chosen zeolite for the adsorption to take place under offshore operating conditions by using natural gas comprising of methane as a feed stream will be discovered throughout the experimental works. Other than that, the research is carried out in order to analyze the isotherm and kinetic models about water adsorption on the zeolites and thus to compare with other research about the models.

4. SCOPE OF STUDY

The dehydration process will be carried out by using Gas Adsorption Separation Unit (GASU) whereby the model will be valid for measuring the humidity level in the gas stream. The aspects being studied and under investigation throughout the research project are:

a. Characterization and analyzed of the new modified zeolite:
   - Several methods involved in the characterization of zeolite are Scanning Electron Microscope (SEM), Fourier Transform Infra Red Spectrometer (FTIR), and Brunauer-Emmett-Teller (BET)
   - Pore size, surface area, pore volumes and other subjects will be determined through the characterization method

b. Experimental
   - The experiment will be carried out by using different pressures and temperatures. The pressure range is from 10 to 80 bars and the

temperature range is from 10 to 70°C which the experiment will be conducted at offshore operating condition. The relationship between the pressure, and the temperature with the water collected is considered in this present study.

- The estimation of water collection throughout the adsorption process will be done by differentiate the mass before and after of the zeolite.

c. Analyze for dual phase multi-component isotherm and kinetic models of the adsorption process:
   - Isotherms that will be analyzed for the research are Langmuir, and Freundlich.
   - Kinetic models that will be analyzed for natural gas dehydration are Pseudo first Order, and Pseudo second order.

5. RELEVANCY AND FEASIBILITY

The project is relevant with current technology as adsorption has become a major unit operation in chemical and petrochemical industries. After all, due to its flexibility and many undiscovered and undefined aspects of adsorption, the process has been greatly researched worldwide. Besides that, adsorption by using different types of zeolites as the adsorbents and optimum conditions for adsorption reaction for different methods also has been the focus of the research globally. Plus, according to Cavenati, et.al, 2004, physical adsorption on zeolite has been identified as a potential alternative for dehydration technology due to its capability to reduce emission and environmental effects.

The research project has been planned properly in order to complete the project according to the scope of studies and objective that need to be achieved.

CHAPTER 2

LITERATURE REVIEW

Gas dehydration is the removal of associated water with natural gas in vapor state. The process is about removing water vapor from a gas stream to lower the moisture content until it reach "dew point" temperature at which water will condense from the stream (Farag et.al, 2011). It is essential in upstream operation for ensuring smooth operation of gas transmission pipelines, protecting the pipeline and fulfilling the sale gas specification (Amran et.al, 2012). Dehydration reduces corrosion in the system and prevents the hydrates formation which will reduce gas flow capacity. Thus, to avoid such situations, natural gas must be dehydrated (Rojey A. et.al, 1997).

There are several technologies used for gas dehydration such as absorption, membrane separation, direct cooling and adsorption. However, physical adsorption with zeolite material has been identified as an alternative for dehydration technology.

2.1 Technologies used for Natural Gas Dehydration

There are different techniques to dehydrate natural gas on industrial scale as follows:

2.1.1 Direct Cooling

The process is carry out by cooling down the gas mixture forcing the water vapor to form liquids before being removed from the mixtures. Usually, direct cooling is applied for simultaneous dehydration. The saturated water vapor content of natural gas decreases with increased pressure or decreased pressure. Thus, hot gases saturated with water may be partially dehydrated by direct cooling. The cooling

process must reduce the temperature to the lowest value that the gas will encounter at the prevailing pressure to prevent further condensation of water (Siti Suhaila, 2009). However, direct cooling of natural gas will create formation of methane hydrates. Hence, to prevent the methane hydrates formation, methanol or monoethylenglycol (MEG) is injected as hydrate inhibitors before each cooling. Energy consumption of the process is limited and makes them useful for high contaminant's levels. However, direct cooling comes with disadvantages as at higher contaminant's level, the process needs large size of the installations due to intensive energy requirements and large capital costs.

2.1.2 Absorption

Currently, absorption is the most accepted method of natural gas dehydration due to some advantages such as low vapor pressure, high boiling points, low solubility in and of natural gas, and their high hygroscopicity. The water in the gas stream is absorbed in the lean solvent, producing a rich solvent stream which one containing more water and a dry gas (Mamun, 2005). Absorption involves the use of a liquid desiccant to remove water vapor from the gas (Siti Suhaila, 2009).Absorption process solvent types are ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T_4EG). Water and the glycols show complete mutual solubility in the liquid phase due to hydrogen-oxygen bonds, and their water vapor pressures are very low. However, glycol dehydration has several drawbacks including glycol losses due to carryover, foaming, flooding, glycol decomposition and the hazardous environmental effects of VOCs emission (P. Gandhidasan et.al. 2001).

2.1.3 Membrane Separation

Membrane separationsare thin barriers that allow selective permeation of certain gases. In the process of dehydration, the dried natural gas is going through a membrane leaving particles of water and impurities on its surface. Industrial applications of dehydration by gas permeation are currently very limited (Mohammed Mamun, 2005). Membranes for separation are usually formed as hollow fibers arranged in the tube-and-shell configuration, or as flat sheets, which are typically packaged as spiral-wound modules. Membrane separation does not require a separating agent, thus no regeneration is required. Plus, the method is low maintenance requirement because there are no moving parts in the membrane and modular design of the unit allows optimization of process arrangement by using multi-stage operation (Sam Wong & Rob Bioletti, 2013). However, membrane permeation has it owns disadvantages and limitations which are hydrocarbons dew point control, cannot withstand high pressure and temperature, and requires additional processing steps in order to protect the membrane.

2.1.4 Adsorption

Adsorption uses a solid phase with large surface area, which selectively retains the components to be separated. Adsorption dehydration is the process where a solid desiccant is used for the removal of water vapor from a gas stream. The solid desiccants commonly used for gas dehydration are those that can be regenerated and, consequently, used for several adsorption-desorption cycles (Hassan A.A. Farag, 2011). The adsorbents are generally characterized by a micro porous structure which affords a very large specific surface area. Adsorption processes are generally applied when a high purity is required for the processed gas. Because of the risks of erosion of adsorbent particles due to friction and collisions during movement, adsorbents are normally used in fixed beds with periodic sequencing. Adsorption is capable to reduce the emission and environmental effects. Generally, adsorption dehydration is based on selectivity difference of a gas mixture on a micro porous surface. When a

gaseous mixture is exposed to an adsorbent within sufficient time, there will be equilibrium between the gas phase and the adsorbent phase (N. N. Amran et al, 2012).

2.2 Adsorption

In this project, adsorption which is also known as solid bed by using molecular sieve is been used. Wet gas enters into an inlet separator to insure removal of contaminants and free water. The gas stream is then directed into an adsorption tower where the water is adsorbed by the desiccant or zeolite. When the adsorption tower approaches equilibrium, the gas stream automatically switched to another tower allowing the first tower to be regenerated. For good dehydration, the bed should be switched to regeneration just before the water content of outlet gas reaches an unacceptable level or known on the breakthrough condition. The regeneration of the bed consists of circulating hot dehydrated gas to strip the adsorbed water, then circulating cold gas to cool the bed down.

Generally, adsorption is the process where a solid desiccant is used for the removal of water vapor from a gas stream. There are two types of adsorption mechanisms which are physical and chemical adsorption. Physical adsorbent is been used in this project as it allows physical adsorption hold the adsorbate on their surface by surface forces. Adsorption has become a competitive operation that offers alternative to other separation processes such as distillation or liquid-liquid extraction.

Over all the technologies, adsorption separation attracts more interest according to:

i. Low energy requirement
ii. Low operating cost
iii. Ease of applicability over a relatively wide range of operating conditions (such as temperature and pressure)

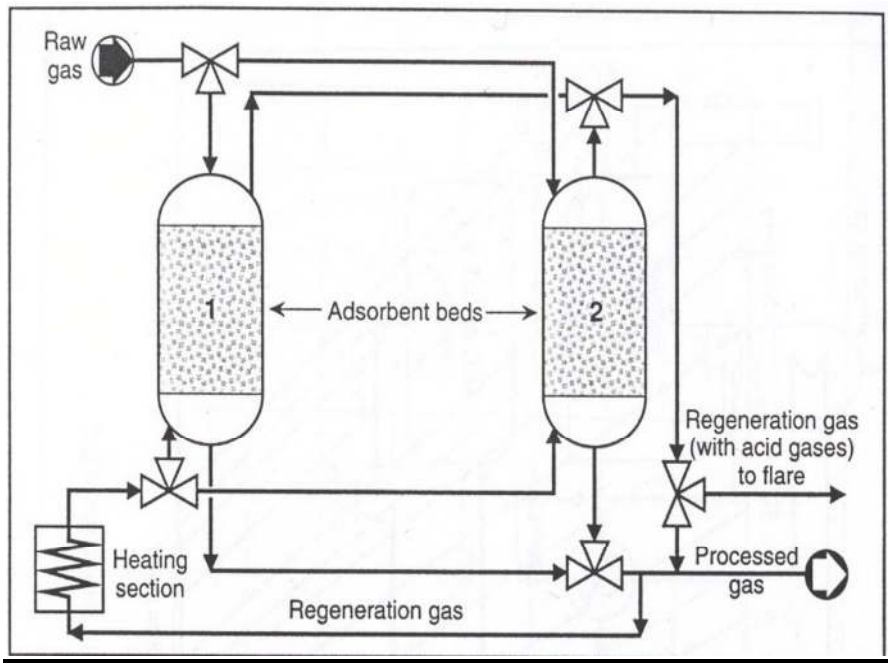


Figure 2: Dehydration by adsorption (reprinted from Rojey A. et.al., 1997)

During normal operation in the drying or adsorption cycle, three separate zones exist in the bed which is:

i. Equilibrium zone where the desiccant is saturated with water or has reached equilibrium water capacity based on inlet gas conditions and has no further capacity to absorb water

ii. Mass transfer zone (MTZ) virtually all of the mass transfer takes place in the MTZ, a concentration gradient exists across the MTZ

iii. Active zone where the desiccant has its full capacity for water vapor removal and contains only amount that amount of residual water left from regeneration cycle

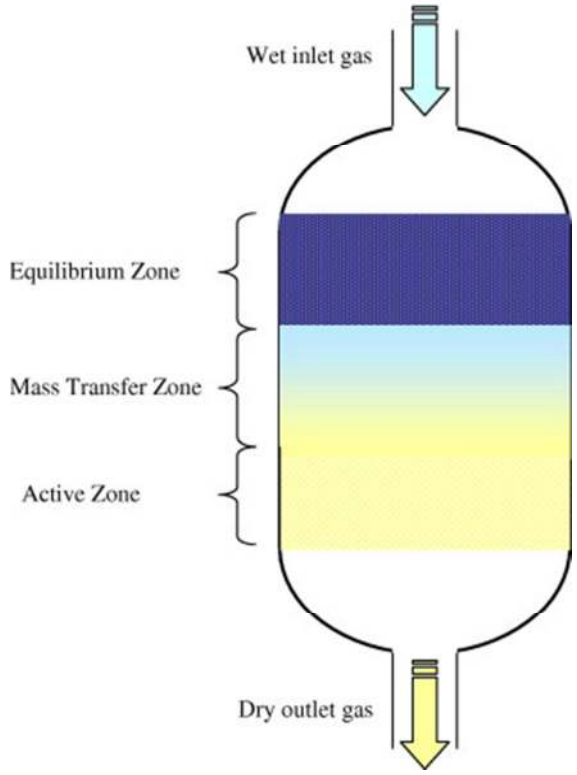


Figure 3: Basic behavior of an adsorbent bed in gas dehydration (Hassan, et.al, 2011)

In experiment carried out by Hassan, et.al, 2011 , 13X molecular sieves with higher capacity than 5A shows closer to ideal adsorption behavior. Mass transfer rate is controlled by pore diffusion (Charles, et.al, 2003).

2.3 Zeolite

Zeolites are called "molecular sieve" because they offer the possibility of gas separation by preventing certain components of a gas mixture from entering the zeolite pores according to the size of the components, whereas the other components enter the pores and adsorbed. Zeolites can be in pellet, beads, or powder. Factor affecting the water adsorption on zeolites is interaction of the permanent and large dipole moment of water with a zeolite cation. The commercial zeolites are 3A, 4A, 5A, and 13X. in order to evaluate the dehydration capacity for these adsorbent

materials, the performance of these materials has been evaluated through nitrogen and carbon dioxide physical adsorption and equilibrium adsorption using BET.

Water adsorption in zeolites is based on physisorption. The main driving force for adsorption is the high polar surface within the pores. This unique characteristic distinguishes zeolites from other commercially available adsorbents, enabling an extremely high adsorption capacity for water vapor and other polar components even at very low concentrations (Hassan, et.al, 2011).

Zeolite played a major role in the development of adsorption method. Essentially, dry air can be readily obtained with zeolite (4A or 5A) as the desiccants (Gorbach, et.al, 2004). Marian Simo, et.al, 2009 equilibrium studies have shown that 3A zeoltie adsorbed a significant amount of water. According to Eva Csanyi, 2011, zeolite NaA provides a reasonably good reproduction of the experimental loadings for water at T=298K. The present study concerns the measurement of equilibrium adsorption of a binary gas mixture of CO_2 and H_2O vapor in trace levels in an inert gas on 13X (NaX) zeolite as adsorbents (Rege & Yang, 2001).

The three major areas of application are:

i. Removal of trace or dilute impurities from gas
ii. Separation of bulk gas mixtures
iii. Gas analysis

There are three basic materials that are used most commonly because they possess these characteristics in a satisfactory manner:

a) Activated alumina
b) Silica gel and silica-alumina gel
c) Molecular sieves

The following are desirable properties of adsorbents used in gas dehydration:

i. Large surface area for high capacity

ii. Good "activity" for the components to be removed, and good "activity" retention with time/use

iii. High mass transfer rate/ high rate of removal

Solid Desiccants	Surface area, m^2/g	Pore volume m^3/g	Pore Dim. Nm.	Density kg/m^3	Cont. Red. ppmv	Reg. temp ^oC
Activated alumina	280	0.4	2-4	720-820	1	150-220
Silica gel	550-800	0.35-0.5	2.5	720-800	10	150-250
Mol. Sieves/ zeolites	650-800	0.27	3-5	690-720	1	200-300

Table 2: Physical characteristics of most favorable solid desiccants used in natural gas dehydration

Milton, 1962, had studied the adsorption capacity of zeolites, silica gel and activated alumina regarding to the water removal efficiency. Milton found that molecular sieve 4A has high performance and efficiency compared to other solid desiccants. The adsorption isotherm studies also shows that molecular sieve 4A adsorbs water much faster than other adsorbents and it elevated for higher values of water adsorbed compared to silica gel and activated alumina. Thus, adsorption rate is also higher.

The effectiveness of parameter of water adsorption on molecular sieve was investigated to find optimum operating conditions. The obtained experimental breakthrough curves were fitted to theoretical models in order to establish the main mechanisms of mass transfer (Hassan, et.al, 2011). Molecular sieves exhibit intra-particular diffusion, which is specifically controlled by molecular diffusion (Carmo & Gubulin, 1997).

Table 3: Zeolites used in research

Adsorbent	Process	Conditions	Authors
3A	Natural Gas Dehydration	30˚C or lower (pressure 20mPa)	Hassan A.A. Farag, Mustafa Mohamed Ezzat, Hoda Amer, Adel William Nashed; (2011)
3A and 4A	Natural Gas Dehydration	25-60˚C and pressures up to 80bar for methane and 25mbar for water vapor	N.N. Amran, A.M. Shariff, K.K. Lau (2011)
4A	Natural Gas Dehydration	Low operating conditions	Gorbach et. al. (2004)
13X, alumina and zeolite X, activated carbon composite	Natural Gas Dehydration	Low and laboratory operating conditions	Kim et al. (2003)
13X, alumina, and natural zeolite	Air impurities such as H_2O, CO_2 and light hydrocarbons	Low and laboratory operating conditions	Rege et al. (2000)

From the above table, it shows some type of zeolites that had been used in past research. Those are the common zeolites that suitable for natural gas dehydration. Thus, throughout the experiment, characterization of the chosen zeolite will be done in order to know the characteristics of the zeolite compared with the commercial zeolites.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

As the project is mainly an empirical research, the results obtained from this research can be used to compare with other literature results. Besides the result obtained from this research using different configuration of zeolite and the offshore operating condition to carry out the process can be used as a basis of comparison with other researches done and real operating condition. The results can hence further enhance the research and development of dehydration of natural gas on zeolite.

3.2 Project Activities

The project activities in this paper are mainly involves in experimental work. After thorough literature review is done, experimental works can be conducted to investigate the two factors mentioned above and the results obtained can be used to compare with the literature readings to analyze the capability of zeolite on adsorption under offshore operating condition.

The figure below shows the general experimental procedures that will be implemented in this research project:

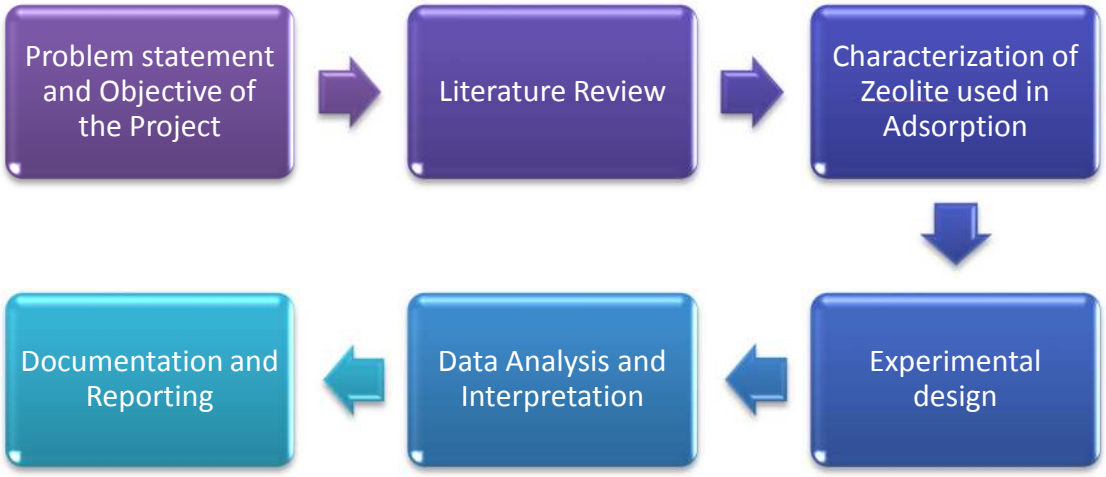


Figure 4: The schematic diagram depicting the general approach throughout the project

3.2.1 Raw Materials and Chemicals Needed

In the experiments that are going to carry out, several raw materials are needed. There are:

i. Methane Gas (CH_4) as the feed stream
ii. Zeolite as the adsorbate
    In this experiment, molecular sieve type 13X which have been modified is going to be used.
iii. Water vapor

3.2.2 Setup of Separation Unit

The separation unit that will be used is Gas Separation Testing Unit (GACU) available in UTP at CO_2 Pilot Plant.

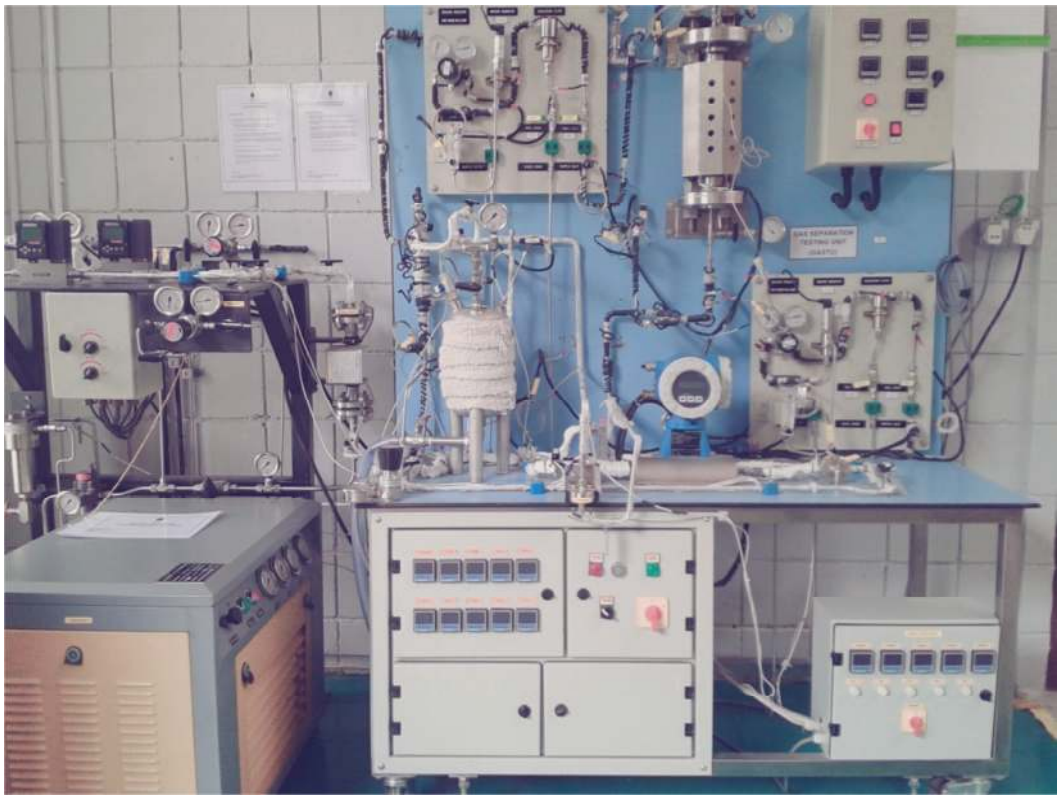


Figure 5: Gas Adsorption Separation Unit (GACU)

Operating Procedures of the GACU:

The inlet gas is compressed until certain level of pressure before being pass through the bubbler where bubbles is introduced. Inlet gas acts as carrier for the water vapor which then flow towards the adsorption tower containing zeolites. After adsorption achieved equilibrium state, the gas will be flow out of the adsorption tower. The inlet and outlet gas will be analyzed in order to measure the gas humidity level. However, before started the experiment, there are some precautions that need to be done:

i) Ensure the moisture analyzer is dry enough by putting it into silica gel to dry it.

ii) Ensure that the adsorbent in the column is totally removed before adding new adsorbent for new experiment.

iii) Ensure the moisture analyzer in fit condition for the experiment to be carried out.

3.2.3 Variation of Factors

As mentioned previously in Chapter 1, there are two subjects that are being investigated. In this context, a characterization lab named BET, FTIR and SEM will be carried out to assist in determining the capability of the zeolite by different pressure applied.

The following ranges of variables were studied during experimental work as to apply with offshore operating condition:

i. The variation of pressure (range: 10 – 80 bars)
ii. The variation of temperature (range: 10 - 70°C)

The following properties were measured during experimental work:

i. The outlet water vapor concentration

3.2.4 Characterization of zeolite used and product of adsorption

Characterization of zeolite is necessary as it can be used as a basis to compare with other types of molecular sieves for adsorption. The fundamental characteristics of zeolites that can be measured through BET method are:

i. Pore size
ii. Surface area
iii. Pore volumes

Whereas for SEM, the characteristics of zeolites that can be investigated are:

i. Size of zeolites that can be studied

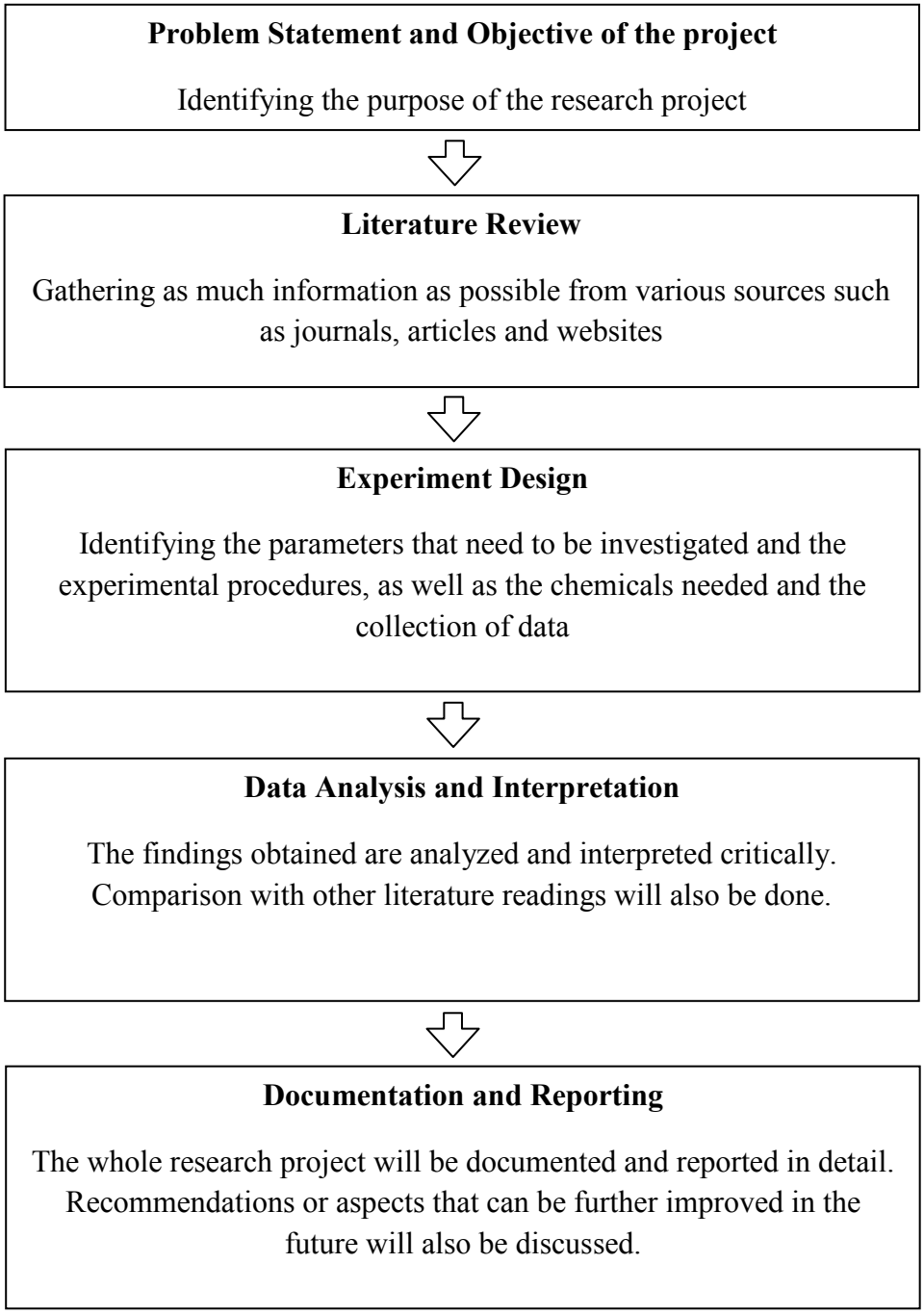
ii. Crystal form by knowing the type of zeolite, aspect ratio and influence on crystal growth
iii. External surface; relative roughness and secondary nucleation effects
iv. Purity of phase; other zeolite types and amorphous material
v. Unknown species; raw material in zeolite can be determined

Characteristics identification through FTIR is:

i. Probe the structure of zeolites and monitor reactions in zeolite pores
ii. Structural information (zeolite lattice)
iii. Information on hydroxyl groups attached to zeolite structures

3.3 Key Milestones

In order to meet the objective of the research project, there are several key milestones that need to be achieved as follow:



3.4 Gantt Chart

No	Detail Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Finalized Project Title																												
2	Literature Review and Understand the Problem Statement																												
3	Determine Types of Zeolite Used In Adsorption																												
4	Characterization of the Zeolite																												
5	Carry out Adsorption Process on the Natural Gas Using Zeolite																												
6	Analyze the Data Obtained																												
7	Compare and Conclude the Results																												

FYP1

FYP2

CHAPTER 4

RESULTS AND DISCUSSION

ZEOLITE CHARACTERIZATION

4.1 Brunauer-Emmet-Teller (BET)

BET surface area analysis by gas adsorption is the most widely used technique to characterize the surface area of solid materials. Adsorption of nitrogen at a temperature of 77K is mostly measured over porous materials. The principle is that at lower pressures gas adsorbs to solids in a monolayer. The analysis can then calculate the surface area covered by this layer based on the number of gas molecules in a monolayer and the dimensions of an individual molecule. Monolayer formation of gas molecules is thus applied to determine the specific surface area, while the principle of capillary condensation can be used to analyze porous characteristics such as pore volume and pore size distribution.

Full BET surface area characterization of disperse, nonporous or macroporous materials pore diameter >50nm (type II isotherms) and mesoporous materials with pore diameter between 2-50 nm (type IV isotherms).

The data from certain sample types such as zeolites, activated carbon, catalysts and various nano-particles often use an alternative theory referred to as the Langmuir equation for the data reduction process. Additional data processing can provide information on mean pore size and pore size distribution of the substrate if sufficient data points are collected.

BET characterization has been made on the zeolite. Figure 8 shows the Langmuir plot for the nitrogen adsorption on the zeolite. The characterization was carried out at temperature of 77K. Below is the result obtained from the BET method which is Langmuir plot, Adsorption/desorption isotherm, and BET plot:

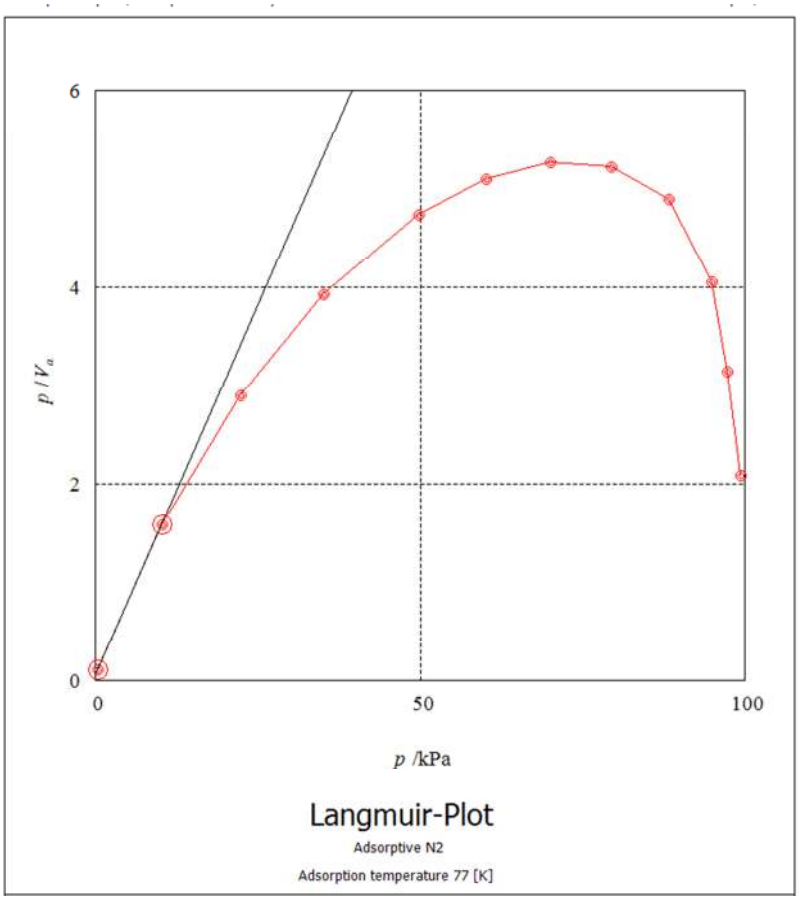


Figure 6: Langmuir Plot

According to the plot above, micropore volume obtained for the zeolite is 6.654 cm^3/g. Whereas the surface area of the zeolite is 28.959 m^2/g.

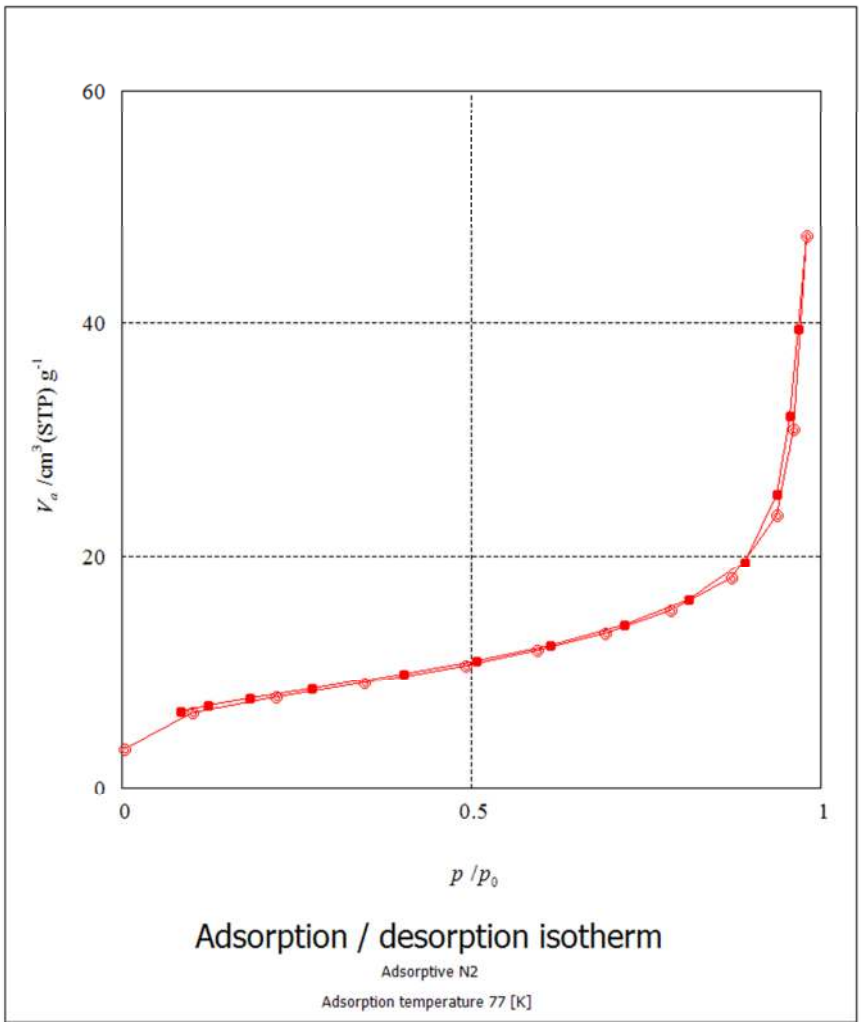


Figure 7: Adsorption/ Desorption isotherm

Adsorption/Desorption isotherm for zeolite has been categorized as Type I isotherms according to Brunauer definition. The curve raises almost vertically, nearly horizontal section and bulk condensation is begin to occur at the end of the adsorption. This is due to micorpore filling that takes place in adsorption process and covered by monolayer adsorption which indicates to Langmuir type adsorption isotherm. Langmuir isotherm is the most widely used which attributed to a pioneer in the study of surface processes. The theoretical basis for Langmuir isotherm is that, adsorption cannot proceed beyond the point at which the adsorbates are one layer thick on the surface (monolayer). The adsorption and desorption rate is independent of the population of neighboring sites and all adsorption sites are equivalent. Referring to the above graph, it shows that the zeolite is a zeolite of type 3A.

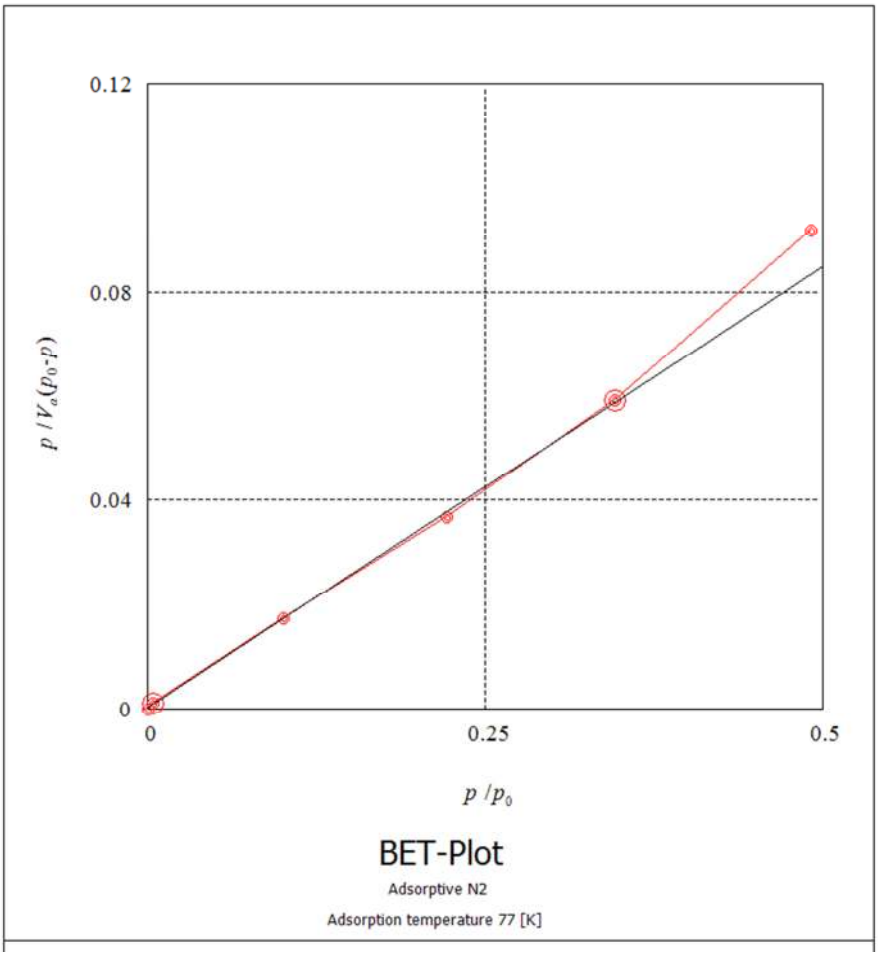


Figure 8: BET-plot

From the characterization, micropore volume is 5.909 cm^3/g, while the surface area is 25.72 m^2/g. While, mean pore diameter for the new modified zeolite is 11.412 nm and the total pore volume of the zeolite is 0.0734 cm^3/g. Both values are greater than the commercial zeolites. According to the literature, total pore volume for commercial 3A zeolite is 0.0073cm^3/g, whereas pore diameter is within the range from 3 to 5 nm. The modified zeolite has larger pore diameter and pore volume which indicates that the chosen zeolite possess high adsorption capacity as compared to commercial 3A zeolite.

Characteristics	Modified 3A Zeolite	Commercial 3A Zeolite
Surface Area (m^2/g)	25.720	38.820
Total Pore Volume (cm^3/g)	0.073	0.0073
Mean Pore Diameter (nm)	11.412	3-5

Figure 9: Comparison between Commercial and Modified 3A Zeolite

Figure 9 shows the comparison between commercial zeolite of 3A with the modified 3A zeolite. The surface area reduced from 38.820 to 25.720 m/g. However, the total pore volume of the modified zeolite is bigger than the commercial by 90% which mean modified zeolite has more pores. Furthermore, mean pore diameter for modified zeolite is 11.412 nm, while for commercial 3A zeoliteis within the range of 3 to 5 nm.

4.2 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) provides topographical and elemental information at magnifications of 10 times to 300,000 times, with virtually unlimited depth of field. Compared with convention Scanning Electron Microscopy (SEM), FESEM produces clearer, less electro statically distorted images with spatial resolution down to 1 ½ nm which is three to six times better.

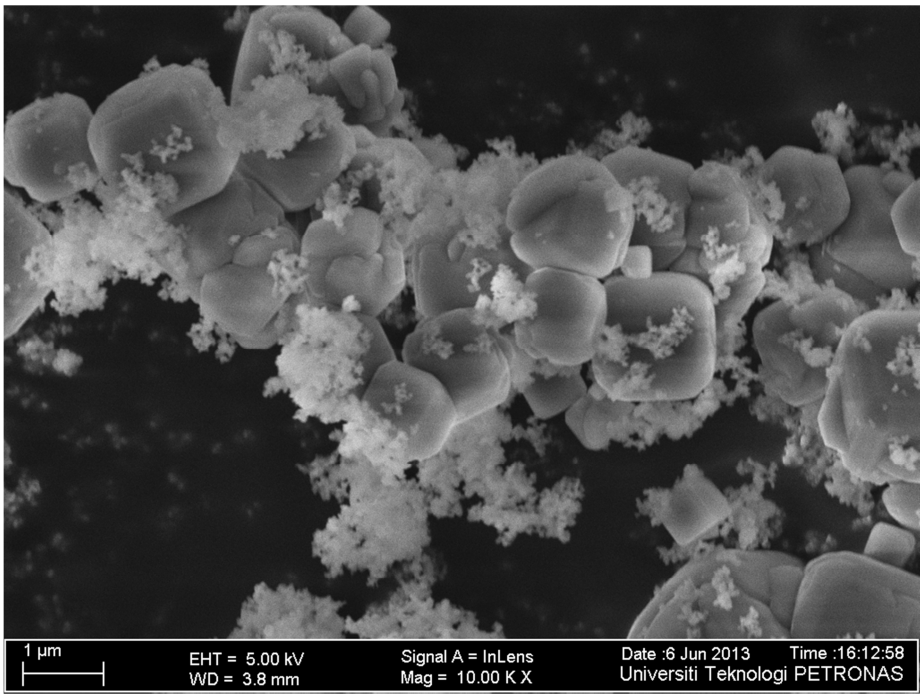


Figure 10: Result 1

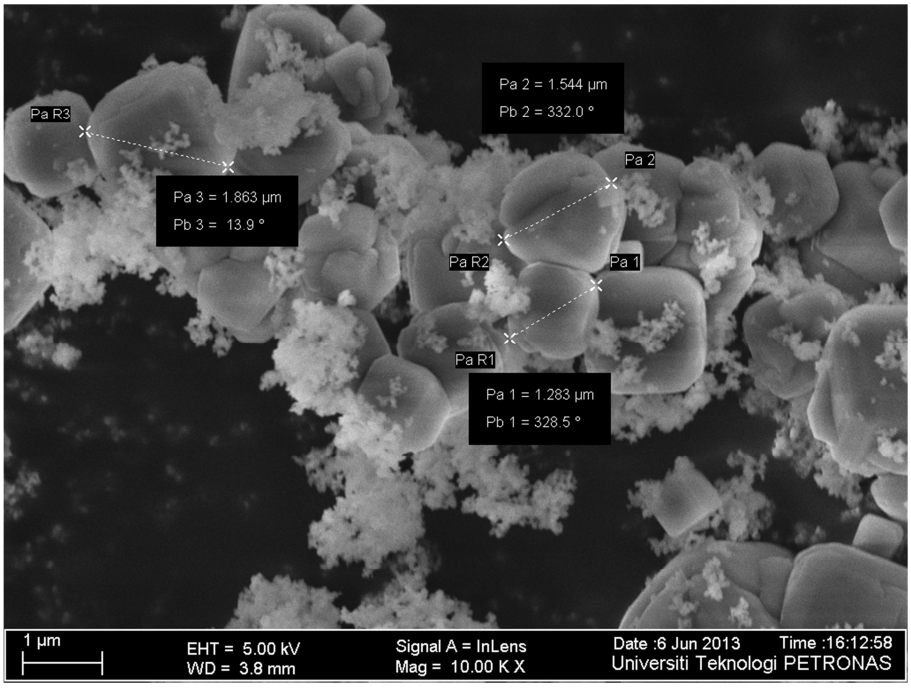


Figure 11: Result 2

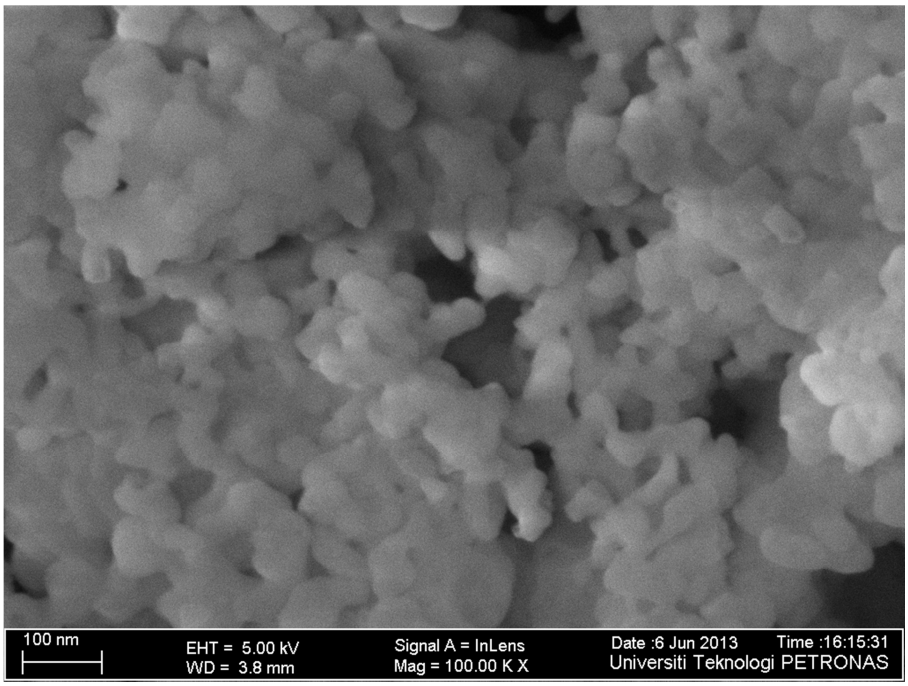


Figure 12: Result 3

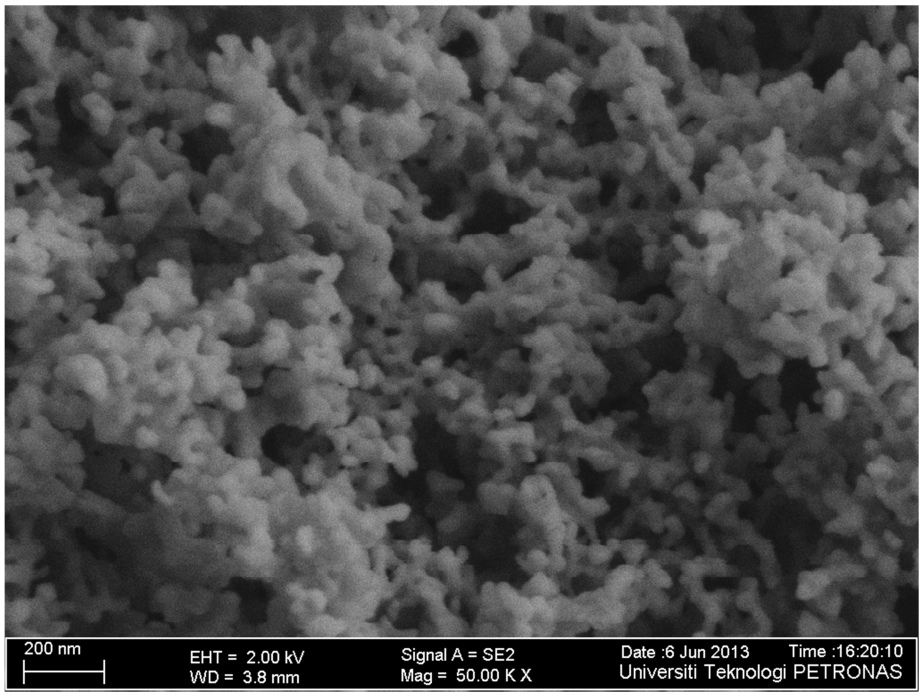


Figure 13: Result 4

Elements	Diameter, µm	Lattice Structure
X	1.863	Cubic-like shapes
Y	1.544	
Z	1.283	

Figure 14: FESEM analysis

Based on the results obtained from FESEM characterization, it shows that the zeolite is made of three different components which has different diameter. Those three elements have diameter of 1.863, 1.544, and 1.283 micrometer respectively. The elements are in cubic-like shapes and the zeolite has lattice structures attached to the elements of the zeolite. Thus, for further information of the types of the element will be known by conducting Fourier Transform Infra Red (FTIR) characterization of the zeolite.

4.3 Fourier Transform Infra Red (FTIR)

Table 4: FTIR analysis

Spectra Region(cm-1)	Transmittance Percentage (%)	Functional Group	Configuration
1384.33	47.6	NO_2 (Nitro compound)	Symmetrical stretch, S
464.21	46.8	Pore	-
571.76	44	Pore	-
871.79	42.8	C-H (alkenes)	Bend, S
1650.88	38	C=C stretch	Alkenes
714.63	37.5	C-H (phenyl ring substitution bands)	Bend, S
		C-H (alkynes)	Bend, B
3435.83	18.8	N-H (amine)	Stretch, M
		O-H (alcohol, phenol)	Stretch, B
1007.40	6	C-O (aldehydes, ketones, carboxylic acids, esters)	Stretch, S

FTIR is an easy way to identify the presence of certain functional groups in a molecule. Also, by using the unique collection of absorption bands, FTIR can be used to confirm the identification of a pure compound or to detect the presence of specific impurities. Hence, zeolite has undergone FTIR analysis and according to Figure 8, there are six elements present in the composition of the zeolite.

DEHYDRATION OF NATURAL GAS

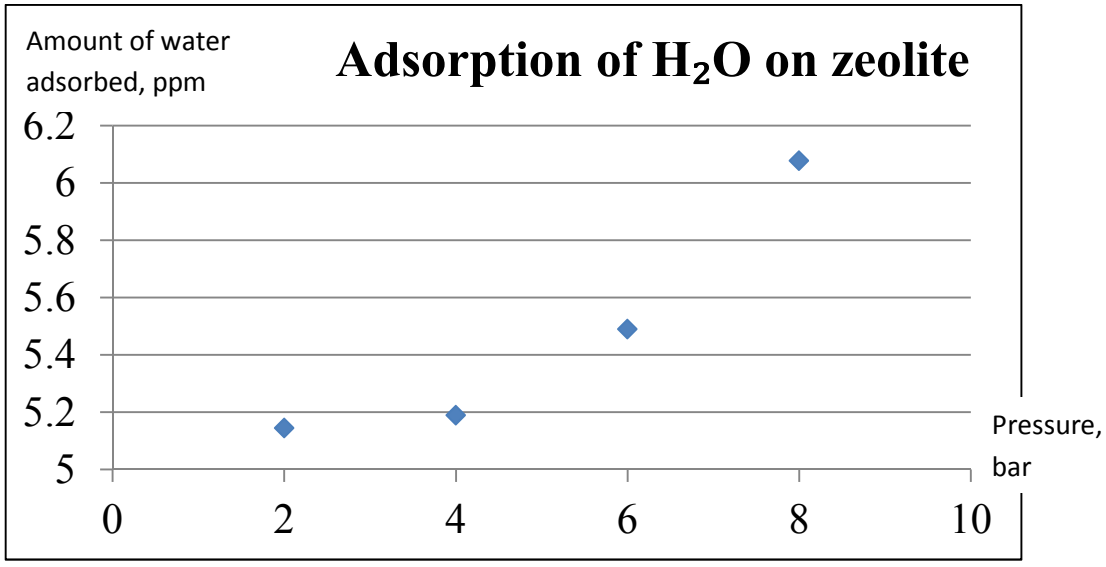


Figure 15: Adsorption of H2O on zeolite

Above figure is the plot between amount of water adsorbed (ppm) versus pressure (bar) at 70 °C. The experiment has been carried out at lower pressure of range from 2 to b bar. Based on the figure, it can be observed that the adsorption capacity increases with pressure. At higher pressure, it would achieve developed stage.

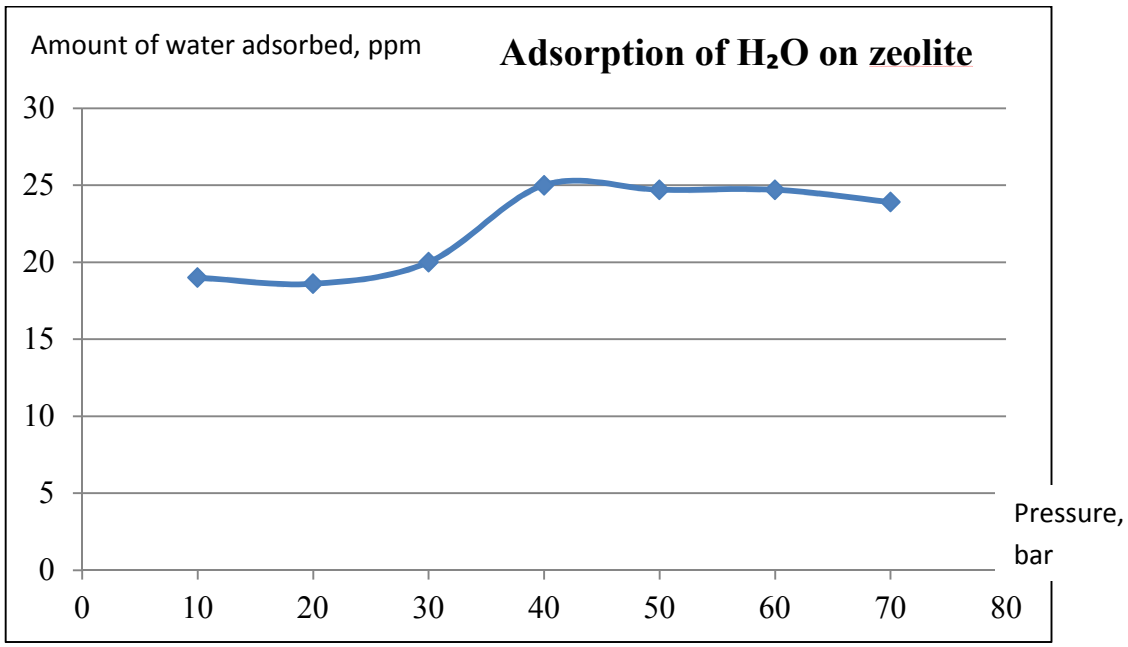


Figure 16: Adsorption of H2O on Zeolite

The experiment has been carried out at higher pressure within the range of 10 to 70 bars at temperature of 70 °C. Although the plot is not so good, but then it can be observed that the adsorption capacity increases as pressure increases. This is due to the fact that three distinct mechanisms contribute to the water adsorption on zeolite where:

i) At low pressure, the water molecules chemisorb to the surface of the adsorbent.

ii) At intermediate pressure, the water molecules then physisorb on the already chemisorbed molecules.

iii) Lastly, with high pressure, capillary condensation occurs within the mesopores and the smaller macropores.

Based on the results obtained, the adsorption capacity of H_2O is higher than CH_4. This phenomenon can be explained by the forces involved in the physical adsorption. Theoretically, there are two forces involved

i) Van Der Waals which always present in any adsorbent-adsorbate system, while

ii) Electrostatic forces only present in adsorbent that has ionic structure such as zeolite.

Furthermore, zeolite has high polar surface that tends to attract polar molecules due to electrostatic forces. Since H_2O has higher polarity compared to CH_4, H_2O tends to be adsorbed at higher capacity by the zeolite material.

CHAPTER 5

CONCLUSION

Thus, it can be concluded the water adsorption on zeolite can take place under a high temperature and pressure as the adsorption capacity increases with pressure. For the zeolite characterization, it has been proved that the chosen modified zeolite has more advantages compared to the commercial one. Based on the results obtained from the characterization, the zeolite capability is higher with the new modified structure.The zeolite possesses high adsorption capacity. Hence, this might favor adsorption to occur at effective rate.

However, for further improvement in the future, the zeolite can undergo further characterization in order to identify whether it is hydrophobic or hydrophilic component. So that, the capability of the zeolite to absorb water can be confirm with valid data. Other than that, the zeolite might undergo Thermalgravimetric Analysis (TGA) in order to know the maximum temperature for the zeolite to withstand.

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APPENDICES